Transactions of the SAEST VOL. 37 No.3&4 July-Dec. 2002 149-151

Effect of Organic Additives on Electrodeposition and Dissolution of Zinc from Zincate Solutions

A. John Rathinam, G. N. K. Ramesh Bapu* and V. S. Muralidharan
Central Electrochemical Research Institute, Karaikudi 630- 006, INDIA

Cyclic voltammetric studies were carried on glassy carbon in 0.12 M ZnO, 2.75 M NaOH containing various concentrations of triethanolamine and furfuraldehyde. The deposition of zinc was found to occur in stepwise electronation. The chemical step followed by first electron transfer was slow. Triethanolamine and furfuraldehyde participated in the electron transfer processes. Triethanolamine adsorbed on the surface and hindered the zinc deposition. Both triethanolamine and furfuraldehyde hindered hydrogen evolution reaction.

Keywords: *Cyclic voltammetry, triethanolamine, furfuraldehyde, zincate bath*

Introduction

Organic compounds are used as additives in zinc plating baths. They affect the nucleation and growth of zinc. They improve the adhesion, grain size and grain homogenization [1]. Cyclic voltammetry was used to study the electrochemical behaviour of noncyanide zinc complexes [2]. Voltammetric studies carried out on platinum from zinc ethanolamine complexes revealed that the complex underwent successive reduction to zinc with the formation of monovalent zinc [3]. The present communication deals with the role of triethanolamine and furfuraldehyde on the deposition and dissolution of zinc from zincate solutions.

Experimental

All solutions were prepared by using analar grade chemicals and double distilled water. An all glass three electrodes cell assembly of 80 ml capacity was used. A glassy carbon (0.07 cm^2), a large platinum foil and saturated calomel electrode were used as working, counter and reference electrodes respectively. Glassy carbon electrodes were precleaned. To minimize IR drop, a finely drawn capillary was used. The desired potentials were swept (5 – 100 mV/sec) using a potentiostat and the response was recorded on X – Y recorder. Experiments were carried out at 30°C in ZnO (0.12 M), NaOH (2.75 M) along with triethanolamine ($0.075 < x > 0.3$ M) and or furfuraldehyde ($0.012 < x > 0.048$ M).

Results and discussions

Cyclic voltammetric study

Zincate solutions

When polarized from – 1200 to – 2000 mV, the forward scan exhibited a cathodic peak at – 1610 mV (Fig. 1). Beyond – 1750 mV, current increased due to hydrogen evolution. When the scan was reversed, the zero current crossing potential (ZCCP) occurred at - 1550 mV. A sharp anodic peak appeared at – 1440 mV. The cathodic peak potentials became active with sweep rates. They varied 50 ± 10 mV/decade of sweep rate. Anodic peak potentials also varied 50 ± 10 mV/ decade change of sweep rate.

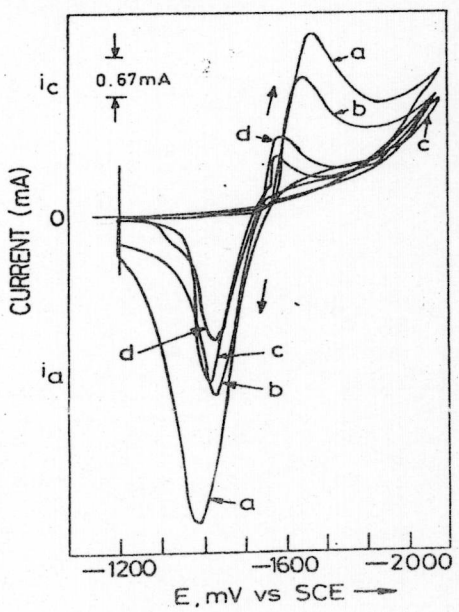

Fig.1. Cyclic voltammograms in 0.12 M ZnO + 2.75 M NaOH solutions at various sweep rates
a) 5 mV/sec b) 10 mV/sec c) 50 mV/sec d) 100 mV/sec

Zincate solutions containing organic compounds

Introduction of organic compounds did not alter the electrochemical spectrum. When the triethanolamine concentration was varied the cathodic peak potentials became active while peak current decreased (Table 1).

* Author for correspondence

0036 - 0678 - 00 /37 - 3 & 4 -149

Table 1: Effect of triethanolamine concentration on the deposition of zinc at 50 mV/sec sweep rate

Concentration (mM)	$E_{p,c}$ (mV/sec)	$I_{p,c}$ (mA)
0	- 1660	1.386
0.075	- 1720	1.089
0.150	- 1740	0.891
0.225	- 1760	0.726
0.300	- 1730	0.957

Anodic peak current and potentials were not significantly affected by triethanolamine concentration. Introduction of furfuraldehyde to zincate solutions did not vary cathodic peak current and potentials (Table 2).

Table 2: Effect of furfuraldehyde concentration on the deposition of zinc at 50 mV/sec sweep rate

Concentration (mM)	$E_{p,c}$ (mV/sec)	$I_{p,c}$ (mA)
0	- 1660	1.386
0.012	- 1690	1.320
0.024	- 1700	1.320
0.036	- 1700	1.320
0.048	- 1690	1.320

In presence of 0.15 mM triethanolamine concentration various amounts of furfuraldehyde were added. Though triethanolamine and furfuraldehyde addition shifted the Ep,c from – 1660 mV to – 1740 mV, concentrations of furfuraldehyde did not affect $E_{p,c}$ (Table 3). However cathodic peak currents increased with furfuraldehyde concentrations.

Table 3: Effect of furfuraldehyde concentration in presence of 0.15 M triethanolamine on the deposition of zinc at 50 mv/sec sweep rate

Concentration (mM)	$E_{p,c}$ (mv/sec)	$I_{p,c}$ (mA)
0	- 1660	1.386
0.012	- 1740	0.860
0.024	- 1740	0.890
0.036	- 1740	0.920
0.048	- 1740	0.940

Deposition of zinc

Under transient polarization conditions, zincate ions may undergo electronation as

$Zn(OH)_4^{2-} \quad Zn(OH)_3^- + OH^-$

$Zn(OH)_3^- + e \quad Zn(OH)_2^- + OH^-$

$Zn(OH)_2^- \Leftrightarrow ZnOH + OH^-$ (slow)

$ZnOH + e \quad Zn + OH^-$

For the above slow step

$$I_c = k_3 k_2 k_1 [Zn(OH)_4]^{2-} (OH^-)^2 \exp - F\Delta\phi/RT$$

As there was a large potential separation between anodic and cathodic peaks, one would write [4, 5]

$$E_{p,c} = E^o + RT/nF[\ln k^o/\sqrt{D} - 0.5 \ln \alpha_c Fv/RT - 0.78]$$

where, $E_{p,c}$ is the cathodic peak potential, n is the sweep rate, D is the diffusion coefficient, α_c is the transfer coefficient. A plot of $E_{p,c}$ vs log υ would give a cathodic Tafel slope. The observed values of 50 ± 10 mV/ decade confirms the chemical step followed by first electronation as slow.

Triethanolamine (TEA) adsorbs on the electrode surface due to the interaction of lone pair of electrons on nitrogen atom. The adsorption caused a decrease in cathodic peak current.

Hydrogen evolution reaction

Figures 2 and 3 present the E – log i_c curves obtained at 10 mV/sec for hydrogen evolution reaction. Presence of TEA and furfuraldehyde in zincate solutions hindered hydrogen evolution. They offer inhibition by adsorbing on the surface. The inhibition was found to increase with TEA and furfuraldehyde concentrations.

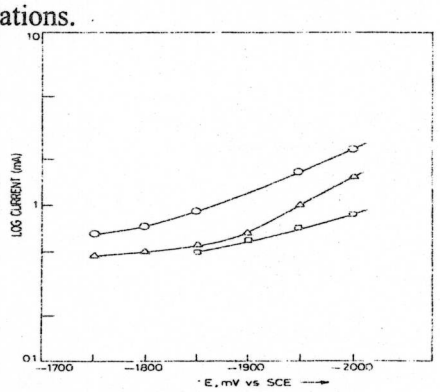

Fig. 2. Effect of triethanolamine concentration on hydrogen evolution reaction (E – log i_c) O-O-O- No TEA; Δ-Δ-Δ - 0.15 mM TEA; □□□ - 0.225 mM TEA

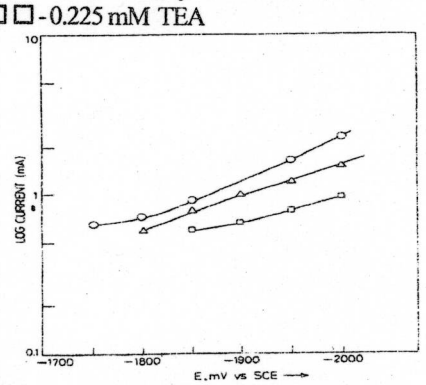

Fig.3. Effect of furfuraldehyde concentration on hydrogen evolution reaction (E – log i_c)

O-O-O	No furfuraldehyde
Δ-Δ-Δ	0.024 mM furfuraldehyde
□□□	0.036 mM furfuraldehyde

Conclusion

Zincate ions undergo electronation successively. The chemical step followed by first electron transfer is the slow step. TEA adsorbed on the electrode surface and hindered the rate of zinc deposition. Presence of TEA and furfuraldehyde in zincate solutions hindered the hydrogen evolution reaction.

References

1. Herb Geduld, *"Zinc Plating"* Finishing Publications Ltd, Teddington, Middlesex, England, 1990.
2. V S Vasantha and V S Muralidharan, *Proc. Indian Acad. Sci* (Chem Sci), 106 (1994) 825.
3. S Shabana Begum, C Sivakumar, S M Mayanna and V S Muralidharan, *Portugalie Electrochim Acta*, 19, (2001) 121.
4. R S Nickolson and I Shain, *Anal Chem*, 36, (1964) 706.
5. D D Macdonald, *"Transient Techniques in Electrochemistry"*, Plenum Press, NY (1997).